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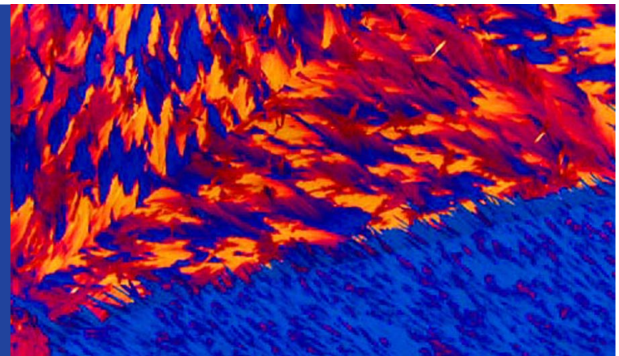

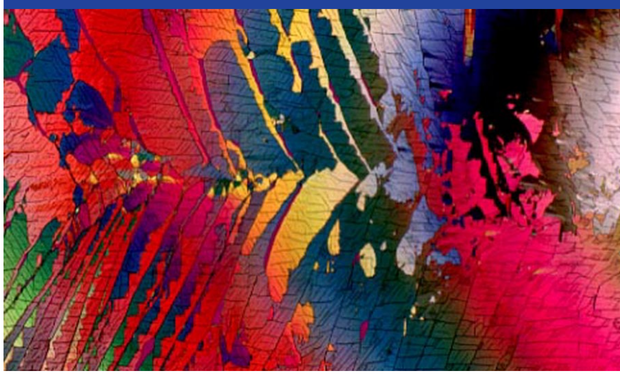

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INTRODUCTION

The term pest derives from the Latin pestis for plague and is used to describe plants (mostly weeds), vertebrates, insects, mites, pathogens and other organisms which occur where we do not want them. Large agricultural endeavors have intensified the problem by concentrating a large population of pests in discrete areas. With the availability of vast quantities of succulent food and often the absence of natural enemies, pests can reproduce quickly and become a serious agricultural problem. Insects, in particular, often exhibit a dramatic and rapid increase in population size under these conditions. The average soil density of insects is about 9 million per acre with about 10 thousand "in flight" above it. The world's main source of food is plants and the animals that rely on plants for their diet. Among the 800,000 species of insects, about 10,000 are plant-eating and add to the devastating loss of crops throughout the world.

Figure 1. (above left) DICHLORAN
Fiqure 2. (above right) MONURON

Equally important are the agricultural crop losses due to weed infestation. Weeds deprive the crops of moisture and nutritive substances from the soil. In some instances they even shade crops and hinder their growth. The use of herbicides in the control of weeds is now a standard practice in the United States, and it has been estimated that we would have 10 to 12 percent of our population working on farms, manually dissecting weeds from the crops, were it not for herbicides.

Microorganisms also contribute heavily to agricultural crop destruction. Most plant diseases can be controlled to some extent with modern synthetic fungicides. In general, fungal plant diseases are basically more difficult to control with chemicals than are insects because the fungus is a plant living in close quarters with its host. This makes it especially arduous to find chemicals which will selectively destroy the fungus without harming the plant. Other organisms that cause plant diseases are viruses, rickettsias, algae, nematodes, and mycoplasma.

Approximately one-third of the world's agricultural food output is destroyed by pests during growth, harvesting, and storage. In the United States alone this amounts to about $20 billion annually despite the heavy use of pesticides and other current control methods. One is tempted to wonder what the losses would be without pesticide use.

Pesticides are a big business with a lot of money at stake. Annually, United States manufacturers produce almost a billion kilograms of synthetic organic pesticides, valued at over $5 billion, with an even higher retail value. More than 50 U.S. firms manufacture pesticides of one type or another, although 14 firms account for about 85 percent of total overall pesticide sales. Although our domestic consumption of pesticides has grown substantially over the past few years, the rest of the world is also using the chemicals at an escalating rate as more countries develop their agricultural and industrial economies.

The effects of pesticides on nontarget organisms and the environment have been a source of bitter controversy. The most easily identified pesticide nontarget consequences were those of the persistent organochlorane insecticides (such as DDT) and their metabolites. These deadly chemicals have devastated populations of certain species of fish and birds. Less readily apparent are the consequences of pesticide residues in food and the environment and effects on humans and domestic animals.

The accompanying selection of photomicrographs represents a small portion of the author's collection entitled *Drugs for Bugs*. Pesticides are generally small organic molecules that exist in the form of a free base. For this reason, they can be easily melted and recrystallized between a microscope slide and coverslip. The unique patterns displayed by recrystallized pesticides are evident in the photo micrographs.

MICROSCOPIC IDENTIFICATION OF PESTICIDES

For the most part, pesticides are composed of small organic molecules that are generally administered in the form of a free base or occasionally as organic salts (1, 2, 3). Because these chemicals are restricted to certain discreet classes, they can often be identified through crossed polarized microscopic examination of recrystallized pesticides. It should be stressed that pesticides are very toxic and extreme caution should be used in their handling. All work should be conducted in a fume hood and microscope slides should have their coverslips sealed with a suitable mounting medium (such as Fisher Scientific, Inc. Permount).

To prepare pesticide crystals for examination in the microscope, deposit a few milligrams of the appropriate pesticide on a glass microscope slide and carefully place a coverslip over the powder. Next, heat the bottom side of the microscope slide carefully with a bunsen burner or hot plate until the powder has completely melted. Some pesticides decompose upon heating and will provide poor subjects for microscopic examination. When

Figure 1. DICHLORAN (top left previous page)
This fungicide is a member of the substituted aromatic class of pesticides derived from the parent compound hexachlorobenzene. These chemicals are useful for seed treatment and in some instances, as a wood preservative. The mechanism of action displayed by this diverse group of pesticides is probably by chemically combining with biological amines and thiols. The fungistatic activity generally results in a reduction of fungi growth rates or interference with sporulation. Dichloran has moderate oral toxicity to animal life and has proven useful in controlling fungal diseases in many fruits, vegetables, ornamental diseases, and field crops. It is particularly effective against the Botrytis, Monilinia, Rhizopus, Sclerotinia, and Sclerotium fungal species.

Figure 2. MONURON (top right previous page)
This herbicide is a member of the substituted urea class of pesticides that are relatively nonselective and are usually applied to the soil as preemergence herbicides. However, some substituted ureas have postemergence uses, while others are active when foliar applied. The ureas are readily absorbed by the roots and rapidly translocated to the upper plant segments, producing phytotoxic symptoms that are most visible in the leaves. The primary site for biological activity appears to be the Hill photosynthetic reaction, although other mechanisms have been postulated. Monuron has been used for preemergence control of broad-leaved and grass weeds to protect crops such as cotton, sugar cane, pineapple, asparagus, and citrus.

melted, the molten chemical will flow underneath the coverslip and fill the entire volume between the coverslip and microscope slide. Either allow the slide to cool slowly before examination or place the melted chemical on the microscope stage and examine the crystallization process occurring. Figure 5 illustrates a slowly crystallizing sample of the insecticide, DDT (dichloro-diphenyl-trichloroethane). This sample is typical of those that crystallize in the form of spherulites. Spherulites are a common crystallization motif that display a 3-dimensional radial growth pattern from a central nucleus.

To obtain an accurate inventory of crystallization patterns, it is advisable to first recrystallize all of the pesticides (and related chemicals) that will be of interest. Next, carefully photograph all of the crystallization patterns that occur in these samples and catalog the photomicrographs by cross-referencing the samples to both crystallization motif and sample type. Many pesticides display unique patterns as is illustrated in Figure 1 for the herbicide, dichloran. Unfortunately, some pesticides display either a common crystallization pattern such as the major spherulite depicted in Figure 7, or crystallize in very small domains that will not allow unique identification.

In my laboratory, we have recrystallized over 150 different pesticides and cataloged the results as described above. We are able to identify, with a microscope, approximately 100 (or two-thirds) of the chemicals. This represents a rapid alternative to Gas Chromatographic (GC) or High Pressure Liquid Chromatographic (HPLC) techniques (5) and can actually be used as a complimentary tool.

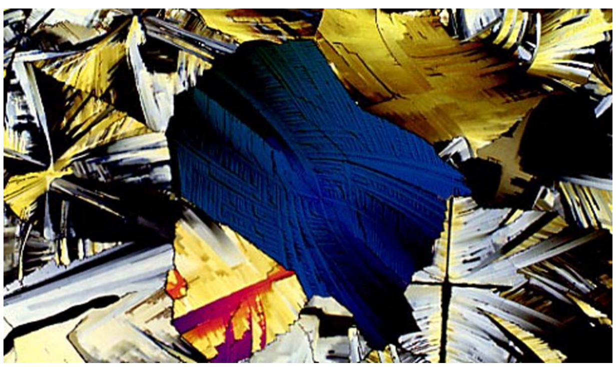


Figure 3. **CARBARYL**
Introduced in 1956, carbaryl was the first carbamate to be successful in the insecticide industry. More of this pesticide has been used worldwide than all other carbamates combined. Carbaryl has two distinct properties that account for its popularity: it has a very low mammalian oral and dermal toxicity and possesses a rather broad spectrum of insect control. This has led to its wide household use as a lawn and garden insecticide. Like the other cabamates, carbaryl antagonizes acetylcholine and competes for binding sites on the enzyme cholinesterase. In agriculture, carbaryl is used as a contact insecticide recommended for use against pests of fruit, vegetables, cotton, and many other crops.

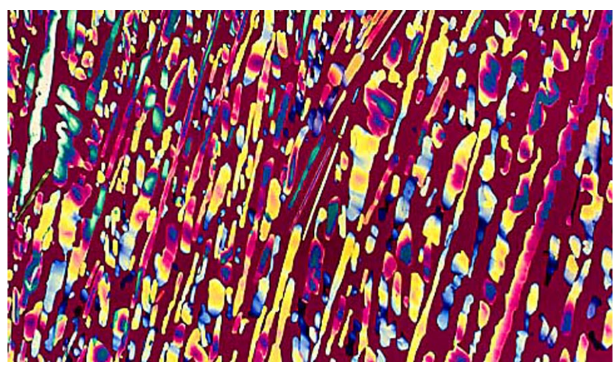
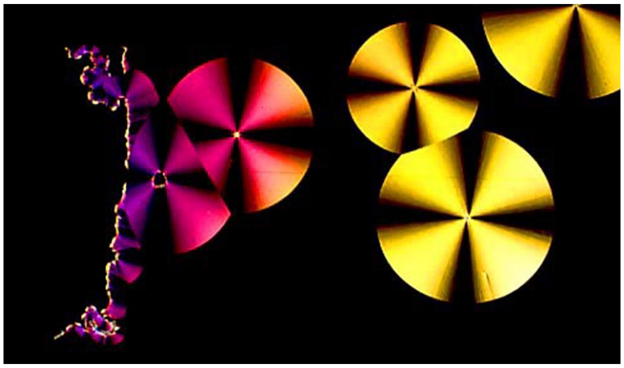


Figure 4. **PARAQUAT**
This powerful defoliant is a member of the bipyridylium class of pesticides. The two most important herbicides in this group are paraquat and diquat, both of which are contact herbicides that damage plant tissues quickly, causing the plants to appear frostbitten because of cell membrane destruction. This rapid degeneration occurs within hours of application, making these novel herbicides also useful as preharvest dessicants for seed crops, cotton, soybeans, sugar cane, and sunflowers. Diaquat is sometimes used in aquatic weed control, and paraquat uses include stubble clearing, pasture renovation, inter-row weed control in vegetable crops, and weed control in plantation crops. Paraquat earned a degree of notoriety several years ago when the U.S. government collaborated with the Mexican government to treat marijuana fields with the defoliant. Many drug users who were exposed to paraquat-laced marijuana developed nose bleeds, headaches, vomiting, and breathing disorders.



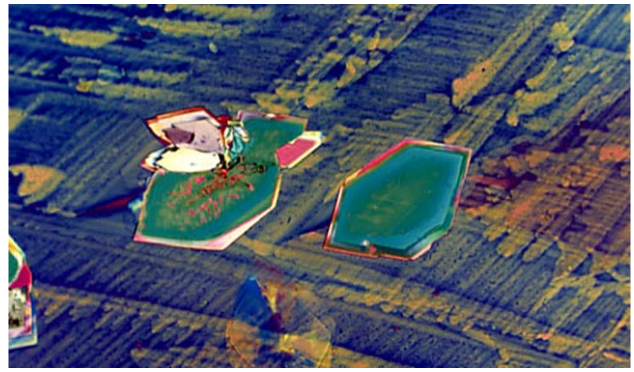
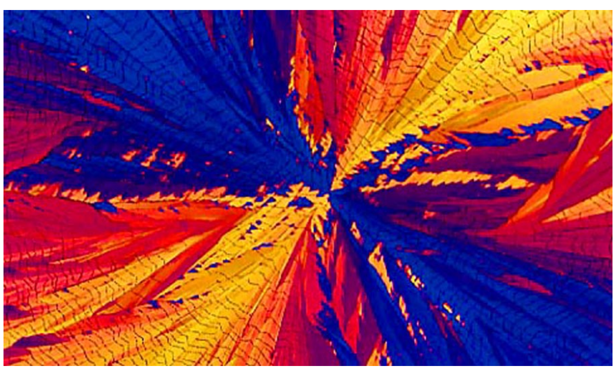


Figure 5 DDT (dichloro-diphenyl-trichloroethane)
This organochlorine insecticide can be considered as the pesticide of the greatest historical significance, due to its effect on the environment, agriculture, and human health. First synthesized by a German graduate student in 1873, it was rediscovered by Dr. Paul Muller, a Swiss entomologist, in 1939 while searching for a long-lasting insecticide for the clothes moth. DDT subsequently proved to be extremely effective against flies and mosquitoes, ultimately leading to the award of the Nobel Prize in medicine for Dr. Muller in 1948. Effective January 1, 1973 the Environmental Protection Agency (EPA) officially canceled all uses of DDT, but not before more than 1 billion kilograms of DDT had been introduced into the United States. Like Endosulfan, DDT disrupts the delicate balance of sodium and potassium within neurons. The pesticide was effective against a wide spectrum of insects in the agricultural arena and also mosquitoes that transmit malaria and yellow fever as well as body lice that carry typhus.

Figure 6. ALDICARB SULFONE
This very toxic insecticide is the sulfone metabolite of the carbamate aldicarb. Unlike most nematicides, aldicarb is provided as a granular powder that significantly reduces the handling hazards. Aldicarb is drilled (spiked) into the soil at planting or during various stages of plant growth. The carbamate is then solubilized by ground water and is absorbed by the roots and translocated throughout the plant, killing both insects that pierce and suck foliage as well as nematodes in and around the roots. The plants oxidize the parent aldicarb carbamate to the sulfone derivative during translocation and it is this species that is responsible for the insecticidal properties. Aldicarb is currently registered for cotton, potatoes, sugar beets, oranges, peaches, peanuts, sweet potatoes, and ornamentals.



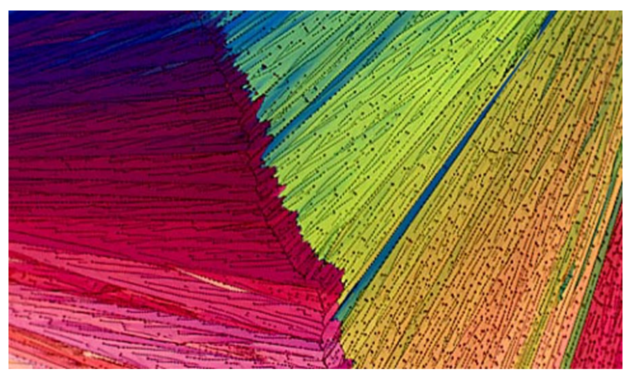


Figure 7. CHLORDANE
This well-known insecticide was the first member of the Cyclodiene class of pesticides introduced in 1945. Other members of this class include Aldrin, Dieldrin, Heptachlor, Endosulfan, and Chlordecone (Kepone). The cyclodienes are persistent insecticides that are very stable in soil and relatively stable to ultraviolet radiation from sunlight. Subsequently, they have been widely used as soil insecticides and for control of termites and soil-borne insects whose immature stages (larvae) feed on the roots of plants. These insecticides are the most effective, long-lasting, economical, and safest termite control agents yet developed. Unfortunately, several soil insects have developed resistance to these chemicals in agriculture, which has resulted in a rapid decline in their use.

Figure 8. DCPA
Chlorthal is the common name given to this arylaliphatic acid by the International Standards Organization, but the herbicide was renamed DCPA by the Weed Society of America. The mechanism of action of arylaliphatic acid pesticides is antagonism of auxin growth hormones. They induce cell elongation and tissue proliferation, produce adventitious roots, modify the arrangement of leaves and other organs, and, in some instances, cause fruit to develop in the absence of fertilization. DCPA is used as a preemergence herbicide recommended for the control of annual weeds in many different crops. It is slowly hydrolzed in soils with-life of about 100 days in most soils.

Figure 9. CAPTAFOL
This useful foliage protectant fungicide is a member of the dicarboximide class of pesticides and was first introduced in 1961. The dicarboximides are some of the safest of all pesticides that are available and are even recommended for lawn and garden use. The mechanism of action in the dicarboximide class appears to be the same for all members of the family. They probably act nonspecifically, although the nature of reactions between fungicides and fungal cell components is not very clearly defined. It is generally believed that thiol or alkylthio groups of fungal metabolic enzymes are most likely in vivo reaction sites. In addition to home use, dicarboximides are utilized primarily as foliage dusts and sprays on fruits, vegetables, and ornamentals.

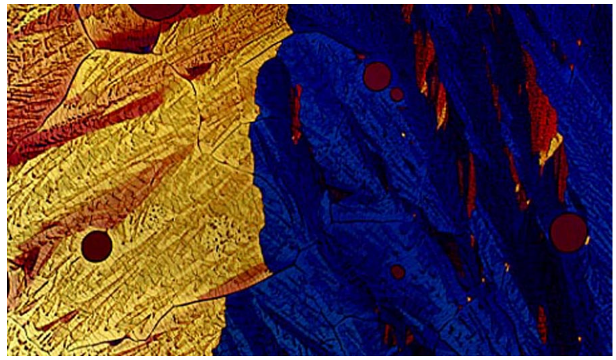


Figure 10. ENDOSULFAN
This powerful insecticide is a member of the organochlorine class of pesticides, fathered by the now banned DDT (dichloro-diphenyl-trichloroethane). It is very closely related chemically to dieldrin, substituting a heterocyclic sulfur in place of the saturated bicyclic ring system. Organochlorines alter both sodium and potassium concentrations in neurons, affecting impulse transmission and causing muscles to twitch spontaneously. Many of the organochlorine insecticides were found to be very toxic to all forms of wildlife early in their use history. Endosulfan earned a bad reputation for an accidential fish kill in the Rhine River in 1969. As a consequence of their extreme toxicity and because they also persist for a long time in the environment, organochlorines are gradually being phased out.

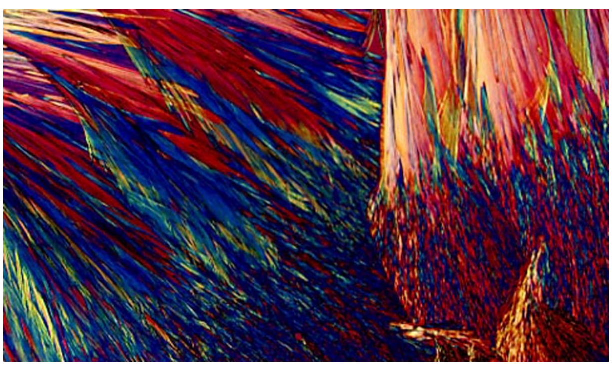


Figure 11. DIAZON
This insecticide is a member of the heterocyclic nitrogen class of pesticides and was introduced commercially in 1952. It subsequently has been marketed under a variety of names. Diazinon is a relatively safe insecticide that has an amazingly good track record around the home. It has been effectively utilized in a wide spectrum of applications, including insects in the home, lawn, garden, ornamentals, around pets, and for fly control in stables and pet quarters. Diazinon has been successfully used in a slow-release formulation that allows the insecticide to volatilize at a lower rate, killing flying and crawling insects in the vicinity.

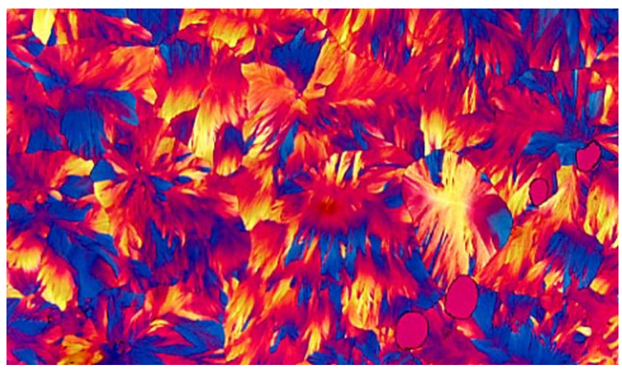


Figure 12. CARBOFURAN
Carbofuran is a member of the carbamate class of pesticides derived from the basic carbamic acid moiety. The mode of action of this pesticide is similar to that of the organophosphates, which act by inhibition of the enzyme cholinesterase. Carbamates were first introduced in 1951 by Geigy Chemical Co. in Switzerland, but found little use due to low effectiveness and relatively high costs. Later studies indicated that the N-methyl carbamates were much more toxic to insects. Carbofuran is a plant systemic and has a high water solubility, which allows the pesticide to be taken into the roots or leaves. It is also a very promising nematicide, being registered as a nematicide for alfalfa, tobacco, peanuts, sugar cane, and possibly effective in soybeans, cotton, grapes, and grains. The carbamate has a relatively short residual lifetime, rendering it useful on forage and vegetable crops.

ABOUT THE AUTHORS

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